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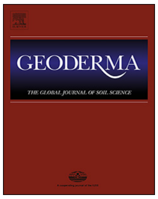

Release of nutrients and organic carbon in different soil types from hydrochar obtained using sugarcane bagasse and vinasse

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ABSTRACT

Hydrothermal carbonization of byproducts from the sugarcane industry generates a solid material (hydrochar) rich in carbon and nutrients with the potential to be used as a soil conditioner. In this context, the objective of this work was to evaluate the nutrient release process from hydrochar with the aim of improving soil quality. To do this, experiments were performed evaluating the concentration of NO_3^-, PO_4^{-3}, K, Ca, Mg, Fe and total organic carbon leached from a column filled with soil and different hydrochar proportions during one month. The proportions of hydrochar were 1 and 4% (w/w) applied to sand, ultisol, and oxisol. Nitrogen and phosphorus were immobilized in the soils due to the high organic carbon released that increase microbial activity and to the presence of iron and aluminum oxides, respectively. The oxisol retains part of the carbon released by the hydrochar due to its high content of silt and clay. Only part of the carbon and nutrients of the hydrochar was released, indicating a recalcitrant material. The prepared hydrochar provided nutrients and organic carbon depending on the soil type to which it was applied. This study shows that hydrochar, if applied in the appropriate proportion, can enhance the soil fertility.

1. Introduction

Hydrothermal carbonization (HTC) has been used as an alternative for the treatment of different biomass residues such as municipal wastes streams (Berge et al., 2011), wheat straw (Reza et al., 2015), tobacco stalks (Cai et al., 2016), and fish waste (Kannan et al., 2016). In the HTC process, biomass with a high moisture content can be used and is converted into a carbonaceous material (hydrochar) at lower temperatures (from 150 to 350 °C) and self-generated pressures (Berge et al., 2011; Chen et al., 2012; Lu et al., 2013; Titirici et al., 2012). Other methods such as pyrolysis have also been used in the conversion of biomass to carbonaceous material. However, pyrolysis needs higher temperatures (from 300 to 1000 °C), a low-oxygen environment, and previously dried biomass (Kambo and Dutta, 2015). Such characteristics require greater energy consumption. Different biomass residues have also been used as raw materials for pyrolysis (Kameyama et al., 2014; Pratiwi et al., 2016; Yuan et al., 2016) and the produced chars shows potential for different applications (Kuppusamy et al., 2016).

Both hydrochar and pyrolytic char have been used as soil conditioners (biochars). The motivation for these uses has its origin in the *Terra Preta de Índio* (TPI), soils which are of global interest due to their intrinsic characteristics (Kambo and Dutta, 2015). TPI has high fertility, is rich in nutrients – mainly calcium, magnesium, and phosphorus – and has a high content of recalcitrant organic matter (Archanjo et al., 2012; Novotny et al., 2009; Pagano et al., 2016). Oliveira et al. (2018) showed that in these soils the C-, Ca- and P-based particles are close in distance to the others (40–70 μm) compared to the surrounding soils in the tropics (hundreds of microns). Thus, this characteristic could provide a greater amount of nutrients and functionalized organic matter to soil capable of increasing the cation exchange capacity (CEC). So, the addition of biochars to the soils aims to reproduce the properties found in TPI (Glaser et al., 2001; Glaser and Birk, 2012; Novotny et al., 2009; Thines et al., 2017). The application of biochars in soils has improved their chemical properties, for example by conferring increased CEC, higher water retention, and increased carbon storage (Beesley et al., 2011; Kelly et al., 2014; Mukherjee and Zimmerman, 2013; Zhao et al., 2013), favoring soil fertility. The release of nutrients and organic carbon from biochar produced with different

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raw materials has been studied by some authors (Riedel et al., 2015; Yuan et al., 2016; Zheng et al., 2013). These studies showed that the nutrient and carbon release was dependent on the conditions of preparation of the material, such as the nature of the biomass and the temperature of carbonization. It was also verified that the soil type in which the biochar was applied can influence the amount of nutrient released due to the interactions between the nutrients of the biochar leachate and the other constituents of the soil (Mukherjee and Zimmerman, 2013).

The possibility of using wet biomass is a major advantage of HTC and it expands the range of raw materials that can be used in this process, such as residues that contain both high moisture and nutrient contents of agricultural interest. Melo et al. (2017b), considering that there is a surplus of sugarcane bagasse and vinasse, proposed the use of these residues from the sugarcane industry as raw materials in HTC. They used phosphoric acid as an additive in order to immobilize the nutrients from the vinasse and from the additive itself. The results showed that the hydrochar produced has potential to be used as an organo-mineral fertilizer. Additionally, Silva et al. (2017) evaluated the effects of acidic (H_2SO_4, H_3PO_4, H_3BO_3), basic (NaOH, KOH), and saline [$FeCl_2$, $(NH_4)_2SO_4$] additives and temperature in the HTC process of the sugarcane bagasse and vinasse mixture. These authors concluded that the additives in the reaction medium can control the incorporation of nutrients into the final product.

Therefore, hydrochar can also contain stable carbon and nutrients, which are essential for soil amendment and carbon storage. Generally, hydrochar is less effective than biochar for carbon storage, because the compounds of carbon from hydrochar increase the microbial activity, which facilitates its degradation (Fang et al., 2018; Malghani et al., 2015). The increase in microbial activity can cause the immobilization of nitrogen (Bargmann et al., 2014; Fang et al., 2018). This immobilization can affect the plant growth. On the other hand, the hydrochar can present some sorbed compounds in its structure such as organic acids, phenols, hydroxymethylfurfural, and furan (Garlapalli et al., 2016; Reza et al., 2014). Some of these compounds may be toxic to the plants and/or soil and the hydrochar should undergo a washing step to remove any excess of toxic compounds to minimize possible contamination. The formation of these compounds varies with the feedstock, reaction time, and temperature employed in the HTC, and thus compositional studies of each material and its application are necessary. For this, a suitable dosage of each type of hydrochar should be studied in order to find the most beneficial proportion to be applied to the soils. In pot experiments with the application of different proportions of hydrochars in the biomass production of spring barley and phaseolus beans, Bargmann et al. (2014) observed an optimal concentration of around 2 to 4% (w/w). However, for all crop species, a hydrochar proportion of 10% led to a decrease in growth. The use of hydrochar in soils may also bring benefits similar to those observed when employing pyrolytic chars, but few studies have been conducted with the objective of showing this. In addition, because the hydrochar obtained from the sugarcane bagasse and vinasse is a new material, to the best of our knowledge, nutrient release studies have not yet been performed.

Thus, the objective of this work was to evaluate the release of nutrients such as nitrogen, phosphorus, potassium, calcium, magnesium, and iron as well as organic carbon from the hydrochar produced using the sugarcane bagasse and vinasse mixture. To do this, experiments were carried out in columns using different proportions of hydrochar in different soil types (ultisol and oxisol). The experiments were conducted with the aim of evaluating the amount of hydrochar necessary according to the soil type, to maximize fertility and minimize the possible negative environmental effects of nutrient excesses.

2. Materials and methods

2.1. Hydrochar preparation and soil sampling

The hydrochar was prepared as previously established by Melo et al. (2017b) and de Melo et al. (2016). Typically, a mixture of sugarcane bagasse, vinasse, and concentrated H_3PO_4 was transferred in a Teflon® closed reactor coated with stainless steel (80 mL maximum capacity) and placed in a muffle furnace with the temperature already stabilized at 230 ± 10 °C. After 13 h of HTC, the reactor was withdrawn and cooled in an ice bath. The hydrochar was separated by vacuum filtration and washed with distilled water until the pH was constant. Then, the hydrochar was dried at 50 °C in an oven until a constant mass was achieved and then sieved at 2 mm.

The soils used in the column experiments, ultisol and oxisol, are predominant soils in the Brazilian territory, and according to their Brazilian classification, these soils are known as “Red-Yellow Ultisol” and “Red Oxisol”, respectively (Embrapa, 2006). The ultisol was collected in São José do Rio Preto, São Paulo state (20° 48′ 19.79″ S and 49° 19′ 43.51″ W), and the oxisol in Maringá, Paraná state (23° 23′ 16.63″ S and 51° 59′ 29.37″ W). The soils were collected from the surface to a depth of 20 cm. The soil samples were dried at room temperature, homogenized, sieved at 2 mm (to remove roots and vegetation), and stored.

2.2. Characterization of soils and hydrochar

The soils and hydrochar were characterized by CHNS elemental analysis using an elemental analyzer (Fisons, EA 1108, USA), with C, H, N, and S being determined directly and O being calculated from the difference between the ash and the total CHNS. Moisture, volatile matter, and ash were determined according to ASTM D1762 (ASTM, 2015). The pH was measured according to EPA 9045D (US EPA, 2015). Functional groups in the hydrochar were analyzed using Attenuated Total Reflectance (ATR) with Fourier Transform Infrared (FTIR) spectroscopy (Perkin Elmer, Spectrum Two UATR, USA), where the spectra were acquired by 20 scans with a resolution of 4 cm^{-1} and spectral range of 4000–400 cm^{-1}. The X-ray diffraction (XRD) pattern was obtained (Bruker, D8 Advance powder, USA) with CuKα radiation ($\lambda = 0.1506$ nm), generated at 40 mA and 40 kV, using steps of 0.02° with a total acquisition time of 1 s per step. Total phosphorus, potassium, calcium, magnesium, and iron were quantified in the soils and the hydrochar previously digested (EPA 3050B) on a hot plate at 95 °C with concentrated HNO_3 (Synth, 65%) and H_2O_2 (Vetec, 30%) (USEPA—United States Environmental Protection Agency, 1996). Also, certified material (Standard Reference Material® 2709a - San Joaquin Soil) was digested for conference of the procedure and the result proved to be satisfactory. The water retention of the hydrochar was evaluated with 0.1 g of material in 100 mL of water in an Erlenmeyer flask on a shaker table. After 24 h, the material was filtered and weighed and the retained water was calculated as the difference between the final wet weight and the dry weight (Wu and Liu, 2008).

2.3. Column leaching experiment

The column leaching experiments were performed in cleaned polychloride vinyl tubes (30.0 cm length × 4.0 cm diameter), closed at the base with a paper and a pierced cap, attached to a funnel with a tube at the end for collecting the leachate samples. The bottom column was kept open to allow for water irrigation. The first 15 cm of the columns was filled with around 245 g of each type of soil: sand, ultisol, and oxisol, in appropriate quantities to reproduce the bulk density of each soil type (1.4, 1.3, and 1.3 g cm^3, respectively). Hydrochar was introduced at the top of each soil column at proportion of 1 and 4% (w/w). A layer of 1 cm of soil was added on top of the hydrochar. A control soil column, without any hydrochar, was tested under the same